Communications received since the end of the Session.

I. "On some Varieties of Tannin." By John Stenhouse, LL.D., F.R.S., F.C.S. Received June 28, 1861.

In two communications "On some Astringent Substances as sources of Pyrogallic Acid," read before the London Chemical Society in the years 1842, 1843, I showed that the usual division of the varieties of tannin into two genera—to wit, those which give black, and those which give green precipitates with salts of iron,—though called in question by Berzelius, is still well-founded: and likewise, that these two genera consist of a great variety of species, which, though closely resembling each other in properties, are still dissimilar in nature; the only instances in which the same species of tannin had been procured from two different plants, being those of nut-galls and sumach. Professor Strecker's important observation made some seven years ago, that grape-sugar is produced when the tannin of gall-nuts is boiled with dilute sulphuric acid, seemed to render a further examination of the varieties of tannin desirable.

Sumach.

As the tannin of Sumach cannot be obtained in such a high state of purity as that of nut-galls by Pelouze's ether process, I was obliged to employ other methods by no means so satisfactory, but which still yield a tolerably pure tannin. A strong decoction of sumach was therefore treated with acetate of lead, which threw down a pale yellow precipitate. This was washed by decantation, and then decomposed by sulphuretted hydrogen and filtered: the filtrate having been boiled with dilute sulphuric acid, on standing for some time, deposited crystals of impure gallic acid. These were collected on a filter, and the mother-liquor, when neutralized with chalk, gave abundant indications of sugar, both by Trommer's test and when subjected to fermentation. A second decoction of sumach, when cold, was treated with sulphuric acid, which threw down a copious precipitate; this when boiled was also resolved into gallic acid and grape-

sugar. This reaction, therefore, in addition to former experiments, serves to confirm the identity of tannin in oak-galls and sumach.

When sumach is long kept, the tannin it contains appears to be resolved in a great measure into gallic acid and grape-sugar, owing to its undergoing a species of natural fermentation. Accordingly under these circumstances when simply boiled with water, sumach emits an odour resembling that of tea, and yields a large quantity of sugar and gallic acid, but mixed with much impurity. Sumach therefore, though it contains much gallic acid, owing to the impurities present in it, is not a good source of that acid.

I may also remark that the amount of tannin in sumach varies considerably, some specimens being very rich and others very poor. This probably arises from the circumstance that the sumach of commerce is the product of various kinds of *Rhus*, such as *Rhus cotinus*, *Rhus coriaria*, &c.

Chinese Galls.

These singularly-shaped galls, which are angular and slightly translucent, have been imported into this country in small quantities for the last fourteen or fifteen years. They are said to be found on the branches of a plant which grows in Japan. From the small amount of the colouring matter they contain, Chinese galls are greatly preferred for the manufacture of gallic acid. Oak-galls, on the other hand, are the best source of pyrogallic acid. The decoction of Chinese galls gave a copious white precipitate with acetate of lead. This was decomposed by sulphuretted hydrogen, and filtered; the clear liquid, when boiled with sulphuric acid, was resolved into gallic acid and grape-sugar, as in the two preceding instances. Another portion of the filtered liquid was evaporated to dryness, and destructively distilled. It yielded a very large quantity of pyrogallic acid. It is clear, therefore, that gall-nuts, Chinese galls, and the various kinds of sumach, contain the same species of tannin.

The Tannin in Tea.

The tannin both of green and black tea is invariably accompanied by a small quantity of gallic acid, which does not arise from the decomposition of the tannin in the tea, as is the case with nut-galls, sumach, or Chinese galls. On treating a strong decoction of tea, when cold, with nearly half its bulk of sulphuric acid, the tannin falls as a

dark brown precipitate. This was collected on a cloth filter, strongly compressed, and washed with a little cold water to free it as much as possible from adhering impurities. The precipitated tannin, when boiled with dilute sulphuric acid, did not yield a trace either of grape-sugar or gallic acid, but was changed into a dark brown substance nearly insoluble in water. It dissolved pretty readily in alcohol, forming a dark brown solution, from which, however, no crystals could be obtained.

Oak-bark from Quercus pedunculata.

A decoction of oak-bark gave a dark brown precipitate with acetate of lead. This was decomposed by sulphuretted hydrogen. The filtered solution, when boiled with sulphuric acid, yielded grape-sugar and a reddish-brown precipitate, but no gallic acid. The reddish-brown precipitate dissolved with difficulty in spirit of wine, but gave no crystals on standing. Rochleder has stated that tea and oak-bark contain the same species of tannin. They certainly resemble each other in their general characters; but as the tannin of oak-bark yields sugar when boiled with dilute sulphuric acid, while that of tea does not yield a trace of sugar, it is clear that the two tannins are not identical.

Valonia, the acorn of the Quercus Ægilops.

This species of tannin, which has a bright yellow colour, when treated in the way already described, yielded sugar, but no gallic acid.

The tannin of pomegranate rind also gave abundant indications of sugar, but no gallic acid.

The tannin of Myrobalans, the fruit of *Terminalia Chebula*, gave similar results.

Tannins which give green precipitates with persalts of Iron.

Salix triandra and *Salix undulata* (the willows generally used for basket making).—A quantity of the bark of these two willows, when boiled with water, yielded a dark brown solution. This, when treated with acetate of lead, gave a copious precipitate of a brownish-yellow colour. This lead-salt was decomposed by sulphuretted hydrogen; and the clear filtered liquid, when boiled with sulphuric acid and

then neutralized with chalk, gave abundant indications of grape-sugar. Another portion of the solution from the decomposed lead-precipitate, when digested with nitric acid, yielded only oxalic acid.

When a decoction of willow-bark is boiled with dilute sulphuric acid, the brown-coloured liquid becomes very red, and a flocculent brownish-red precipitate falls which is nearly insoluble in water, but dissolves pretty readily in hot spirit of wine and in alkaline leys. The brownish-red precipitate, when dissolved in spirit of wine and left to spontaneous evaporation, did not crystallize, but formed a dark brownish resin. It consisted chiefly of impure saliratine, resulting most probably from the decomposition of salicine in solution. When it was digested with nitric acid it yielded a good deal of nitropicric acid. Willow-bark, therefore, is a tolerably good source of this acid.

Alder-bark (Alnus glutinosa).—Alder-bark yields a dark red decoction with water. It was precipitated with acetate of lead, and the lead-salt decomposed with sulphuretted hydrogen. It formed a dark red solution, which on digestion with sulphuric acid yielded no sugar.

Catechu.—It was the light-coloured cubical variety of catechu that I employed. The tannin from this astringent substance, when digested with dilute sulphuric acid, yielded no sugar, a result which corresponds with Neubauer's experiments (Ann. der Chem. und Pharm. vol. xcv. p. 103).

Larch-bark (Pinus larix, *Linn.*).—The bark of the larch is employed in Scotland to some extent in tanning, though the leather made with it is inferior in quality. Larch-bark contains a good deal of a peculiar tannin, which yields olive-green precipitates with salts of iron. The aqueous solution of larch-bark is strongly acid to test-paper, and has at first a pale yellow colour, which exposure to the air renders brownish-red. Acetate of lead threw down a copious yellow precipitate: this was decomposed by sulphuretted hydrogen and boiled with dilute sulphuric acid, when the liquid assumed a fine scarlet colour, like infusion of Brazil-wood. The altered tannin precipitated on cooling in beautiful red flocks, as it is but little soluble in cold water. It is very soluble in alcohol, and its solution has a rich scarlet colour, which is characteristic of this species of tannin. Its alcoholic solution, when left to spontaneous evaporation, did not yield crystals, but formed a dark resinous mass. The clear liquid from which the red flocks were precipitated, when neutralized with

chalk, gave no indications of sugar. Sugar, however, together with a good deal of mucilage and resinous matter, with some larixinic acid, is contained in the crude decoction of larch-bark.

Bark of the common black Mangrove (Rhizophora Mangle *of botanists*).—This species of mangrove-bark is used in tanning, and is occasionally imported into Great Britain for this purpose. It has a brownish-red colour: the colour of its decoction is the same. The tannin it contains is precipitated from its solution both by acetate of lead and concentrated sulphuric acid. When boiled with dilute sulphuric acid no sugar is produced, and the brownish-red precipitate which falls cannot be made to crystallize.

In conclusion, I would observe that it is somewhat remarkable that so many of the tannins which give bluish-black precipitates with persalts of iron are glucosides; whereas of those which give olive-green precipitates with persalts of iron, so far as I know, only one —to wit, the tannin of the willow—is a glucoside.

II. "On Larixinic Acid, a crystallizable volatile principle found in the Bark of the Larch Tree (*Pinus Larix*, Linn.)." By JOHN STENHOUSE, LL.D., F.R.S., F.C.S. Received July 10, 1861.

(Abstract.)

This acid is prepared by digesting larch-bark in water at 80° C., evaporating the infusion at the same temperature to the consistence of syrup, and distilling it in vessels of glass, porcelain, or silver; *i. e.* of a material not liable to be attacked by the acetic acid present in the infusion. The larixinic acid distils over, and partly crystallizes on the inner surface of the receiver, but chiefly remains dissolved in the distilled liquid, which, after being concentrated by cautious evaporation, deposits the impure acid in form of crystals. These are of a brownish-yellow colour; they are to be dissolved and recrystallized, and may be obtained quite pure by sublimation, which takes place at the low temperature of 93° C.

This acid exists as a proximate principle in the larch-bark; most abundantly in that from trees of not more than 20 or 30 years' growth, or from the smaller branches of older trees. When pure, it forms beautifully white crystals, often more than an inch long, of a